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SUPERVISOR'S USE ONLY

TOP SCHOLAR



NEW ZEALAND QUALIFICATIONS AUTHORITY
MANA TOHU MĀTAURANGA O AOTEAROA

Scholarship 2012 Chemistry

9.30 am Saturday 17 November 2012

Time allowed: Three hours

Total marks: 40

Check that the National Student Number (NSN) on your admission slip is the same as the number at the top of this page.

You should answer ALL the questions in this booklet.

Pull out Resource Sheet S-CHEMR from the centre of this booklet.

If you need more room for any answer, use the extra space provided at the back of this booklet.

Check that this booklet has pages 2–24 in the correct order and that none of these pages is blank.

You are advised to spend approximately 35 minutes on each question.

YOU MUST HAND THIS BOOKLET TO THE SUPERVISOR AT THE END OF THE EXAMINATION.

You have three hours to complete this examination.

QUESTION ONE

- (a) (i) Account for the signs and relative magnitudes of the enthalpy changes in the reactions A–F shown below.

A	$\text{Mg}(s) \rightarrow \text{Mg}(g)$	$\Delta H = +147 \text{ kJ mol}^{-1}$
B	$\frac{1}{2}\text{F}_2(g) \rightarrow \text{F}(g)$	$\Delta H = +79 \text{ kJ mol}^{-1}$
C	$\text{Mg}(g) \rightarrow \text{Mg}^+(g) + e^-$	$\Delta H = +744 \text{ kJ mol}^{-1}$
D	$\text{Mg}^+(g) \rightarrow \text{Mg}^{2+}(g) + e^-$	$\Delta H = +1457 \text{ kJ mol}^{-1}$
E	$\text{F}(g) + e^- \rightarrow \text{F}^-(g)$	$\Delta H = -334 \text{ kJ mol}^{-1}$
F	$\text{Mg}^{2+}(g) + 2\text{F}^-(g) \rightarrow \text{MgF}_2(s)$	$\Delta H = -2957 \text{ kJ mol}^{-1}$

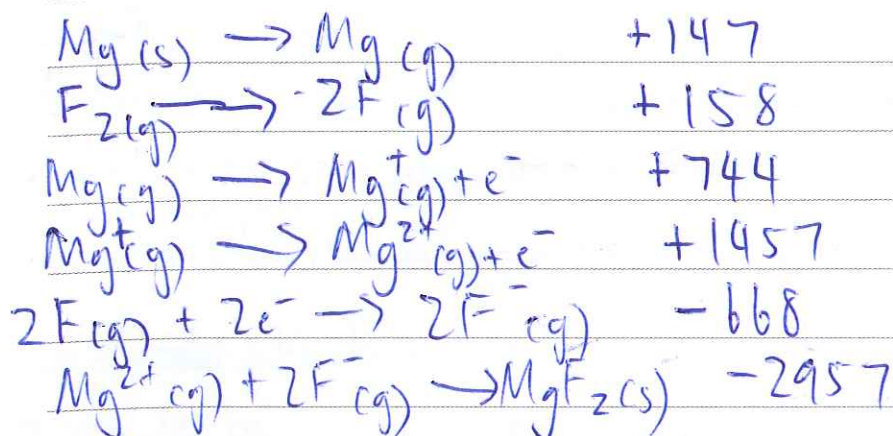
The second ionisation energy of Mg (D) is much more endothermic than the first ionisation energy (C). They are endothermic as energy is needed to ~~be~~ overcome the attraction of the least tightly held electron to the nuclear charge. The second ionisation energy is greater as there is ¹less electrons in Mg^+ compared to Mg and nuclear charge is the same. The ²reduced electron-electron repulsion in Mg^+ means that the ~~valence elect~~ electrons are attracted more strongly to the nucleus, so more energy is needed to ~~break~~ ^{overcome} this attraction.

The ~~top~~ sublimation of Mg (s) in (A) is endothermic as energy is needed to ~~a~~ completely overcome the ~~attraction~~ ~~temporarily~~ metallic bonding of Mg nuclei to turn the solid to a gas. In (B), ~~F₂ has a lower energy~~ energy is needed to break the F-F bond in F_2 to form F, so this is endothermic. The energy needed ~~in~~ for reactions A and B are much lower than the energy for C and D, so the enthalpy changes in A and B are much lower.

(E) is exothermic as F^- has a complete valence energy level and has a lower energy than F , so energy is released and the reaction is exothermic. In (F), the strong electrostatic attractions of Mg^{2+} cations and F^- anions to form a lattice of MgF_2 is strongly exothermic due to the strong ionic bonding formed in the reaction which releases energy. This released energy is much greater than (E), so the enthalpy change is of a much greater magnitude.

- (ii) Explain why the thermodynamic equations given in (i) can be used to determine the enthalpy of formation of magnesium fluoride, and then show how this is done.

This can be calculated using Hess's law which states that the ~~energy~~^{net} enthalpy change of a reaction is the same regardless of pathway taken.



~~Total~~ $\Delta_f H (MgF_2) = -1119 \text{ kJ mol}^{-1}$

(b) For many years the Group 18 elements were known as the inert gases, as a reflection of the belief that they would not form compounds. The synthesis of compounds like XeF_2 , XeF_4 , and XeO_3 showed this belief to be incorrect. The elements are now known as the noble gases, indicating a low, rather than absent, reactivity.

- (i) Using your knowledge of periodic trends, explain why fluorine and oxygen are the elements most likely to combine with xenon, and why xenon is the noble gas most likely to form compounds (apart from radon, which is difficult to work with because of its radioactivity).

~~Fluorine~~ Fluorine and oxygen are the two most ~~electronegative~~ electronegative ~~species~~ elements and so have a very strong tendency to attract electrons to their nuclei. ~~That~~ This ~~result~~ means that it is more likely for F or O to attract ~~an~~ ^{electron} of Xenon and form bonds than another ~~atom~~ ^{element}, which ~~would~~ ~~be~~ ~~easy~~. Xenon has ~~a~~ ~~very~~ more ~~electron~~ ^{greater} energy levels than ~~the~~ Ar, Ne or He so it has ~~more~~ ^{greater} shielding ~~effect~~ ^{effect} acting on its valence electrons. The electrons are thus ~~less~~ ^{less} ~~strongly~~ ^{strongly} attracted to the nuclear charge and can more easily be attracted by F or O to form a ~~bond~~ polar bond and thus a compound.

- (ii) Predict the shapes and approximate bond angles in XeO_3 and $[\text{XeOF}_3]^+$, giving reasons for your answer.

XeO_3 has ~~a~~ four areas of electron density ~~which~~ ~~around~~ central Xe atom ~~which~~ ~~repel~~ which repel as far as possible. One of these electron density areas is non bonding, but still contributes to the shape of the molecule which means XeO_3 has a trigonal pyramidal shape with bonding ~~angles~~ angles of approximately 109.5° .

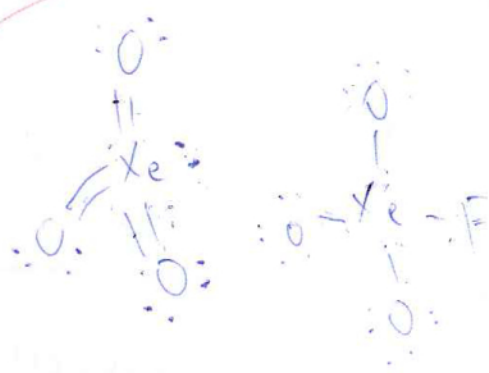
$[\text{XeOF}_3]^+$ has four areas of electron density around central Xe atom, all of these areas are bonding, so ~~and~~ the areas repel as far as possible for a ~~is~~ tetrahedral shape with bonding angles of approximately 109.5° for maximum stability.

- (iii) Discuss the possibility of forming compounds between an element from Group 1 and a noble gas.

Consider whether such a compound is likely to be ionic or covalent and, if such a compound were to exist, state which elements from Group 1 would be the most likely candidates.

They are not very electronegative and so will not attract electrons unlike F or O. So cannot form bonds with Xe unlike F or O.

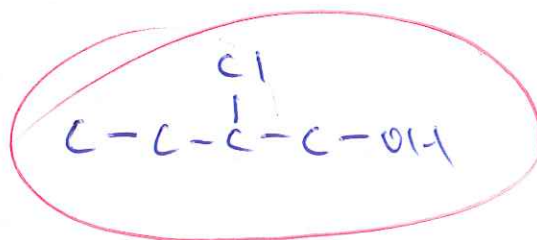
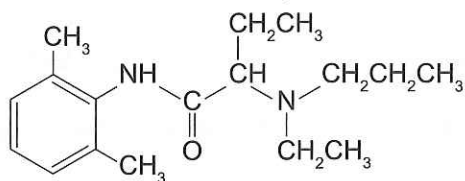
Elements in group 1 has a tendency to lose its 1 valence electron and have a full valence shell for ~~more~~ greater stability. This usually results in ionic bonding as the group 1 elements reacts to form a cation. This is very unlikely to ~~happen~~ react with a noble gas, due to the noble gases having full valence shells and ~~are hence~~ ~~so~~ tend not to accept electrons. ~~The~~ If a ~~real~~ compound were to exist somehow, it would be ionic due to ~~the~~ the group 1 element losing 1 electron and the noble gas gaining one electron for ionic bonding. Li and Na are the more likely candidates due to them having ~~less~~ their valence electrons ~~more~~ closer to their nucleus.



QUESTION TWO

- (a) Etidocaine is used as a local anaesthetic. Its hydrochloride is marketed as Duranest[®].

The structural formula for etidocaine is:



Propose a synthesis for etidocaine, starting with 2,6-dimethylaniline, 2-chlorobutan-1-ol, propan-1-ol and ethanol, and using any appropriate reagents.

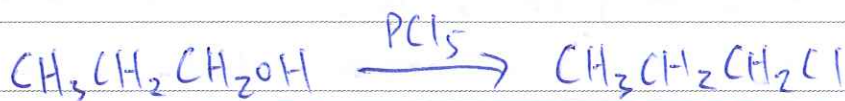
Include structural formulae for each step of the synthetic pathway.

NOTE: Only the amine group of 2,6-dimethylaniline will be active under the conditions you will need for the reaction.

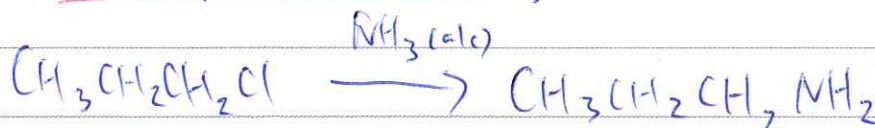


2,6-dimethylaniline

1. React propan-1-ol with PCl₅ to form propan-1-chloropropane



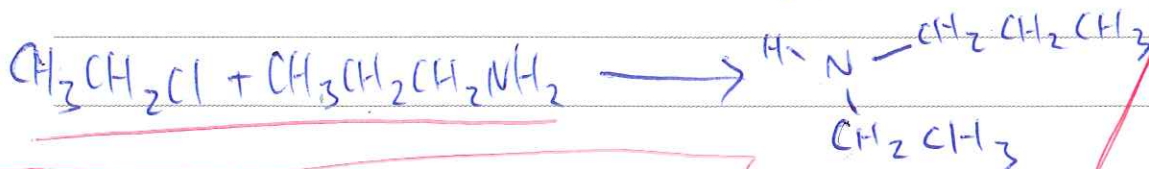
2. React 1-chloropropane with NH₃ (alc) to form 1-amino propane



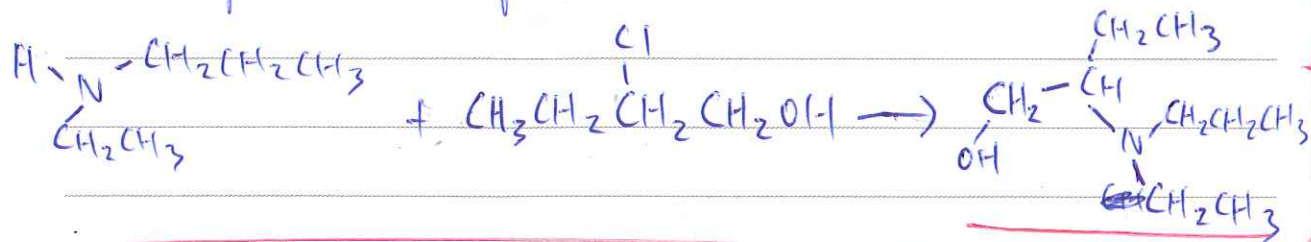
3. React ethanol with PCl₅ to form chloroethane



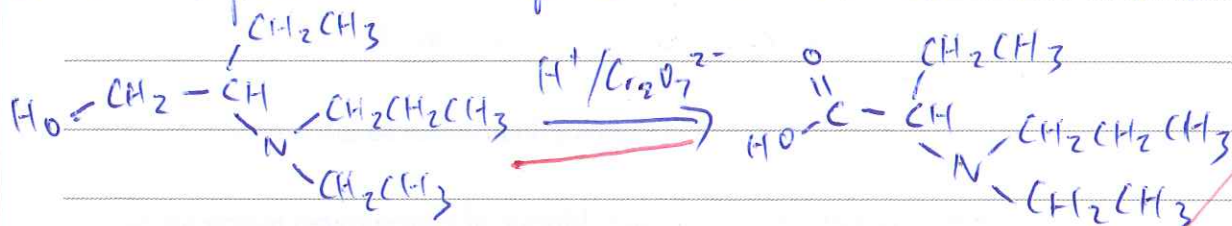
4. React chloroethane with 1-amino propane



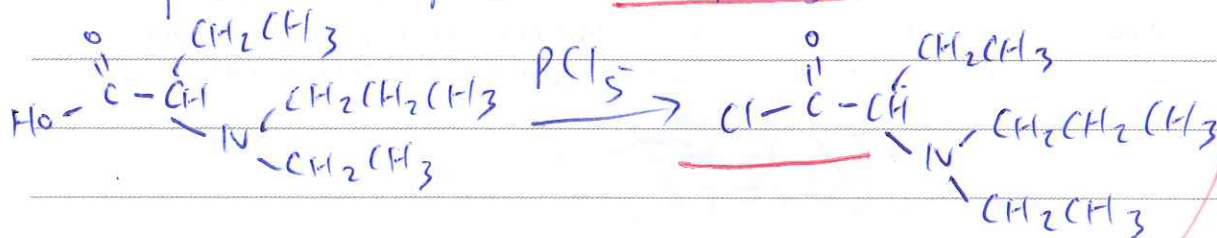
5. React product of step 4 with 2-chlorobutan-1-ol



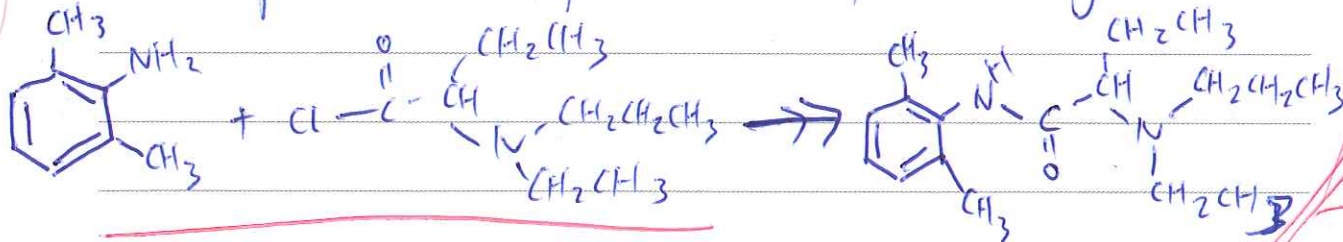
6. React product of step 5 with acidified $\text{Cr}_2\text{O}_7^{2-}$



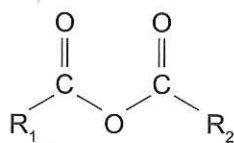
7. React product of step 6 with PCl_5



8. React product of step 7 with 2,6-dimethylaniline



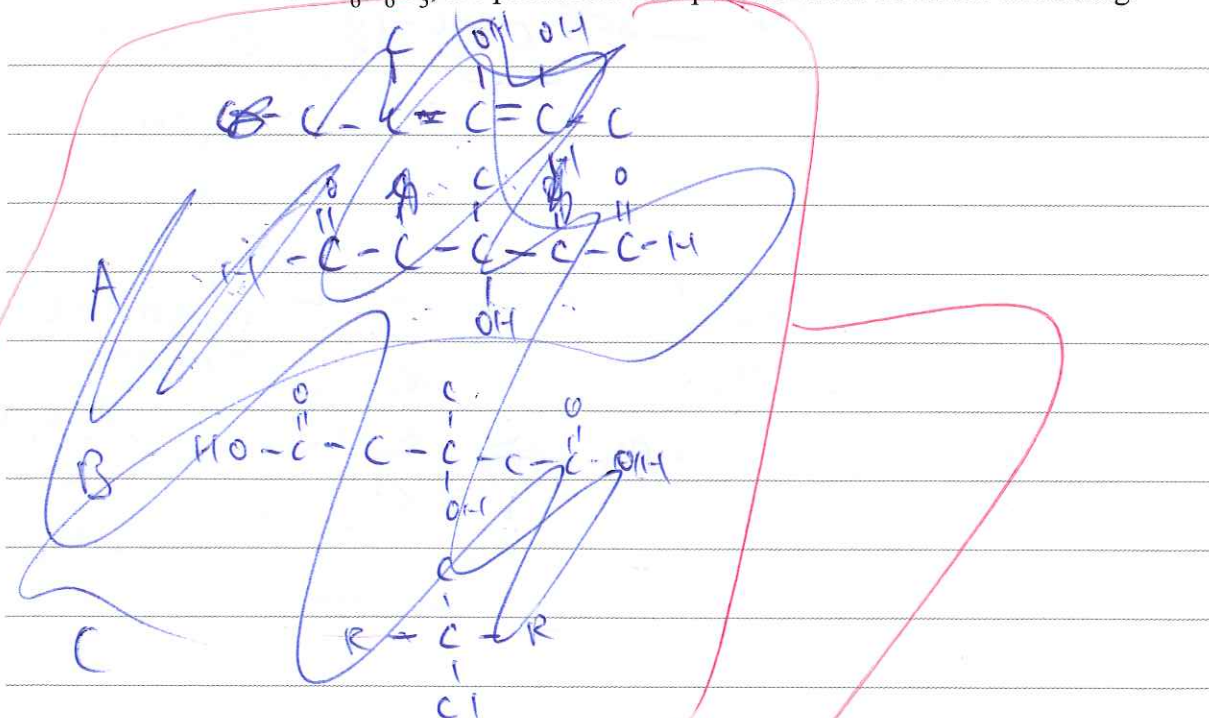
- (b) Acid anhydrides are derivatives of carboxylic acids. Their reactivity makes them useful starting materials for organic synthesis reactions. Acid anhydrides are formed from the condensation reaction between two functional groups.

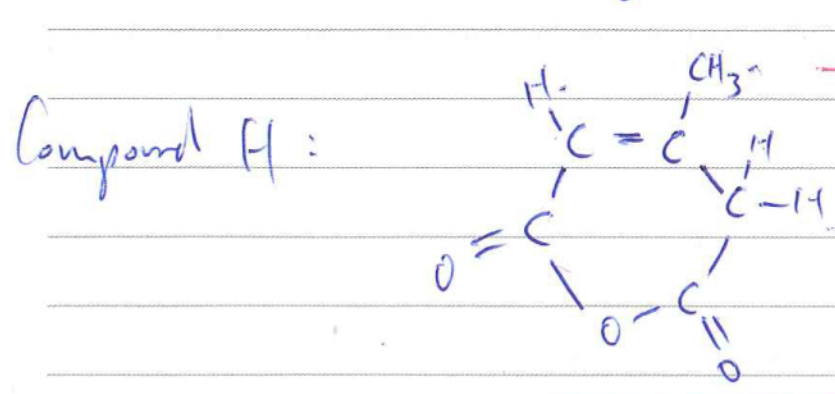
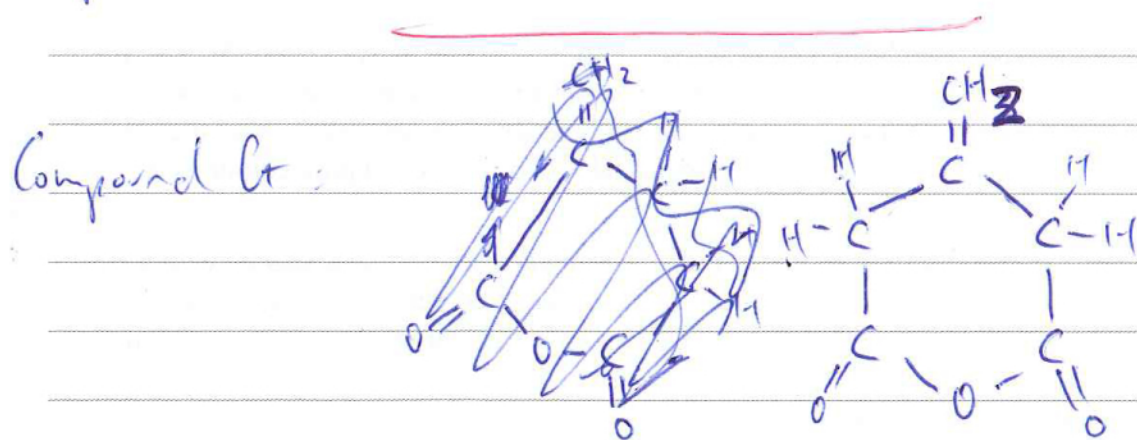
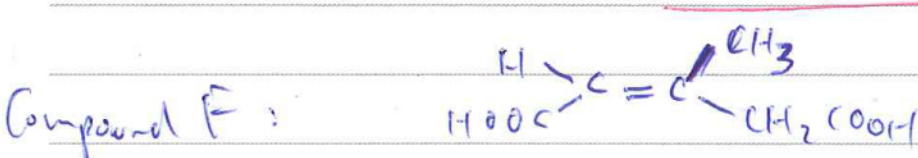
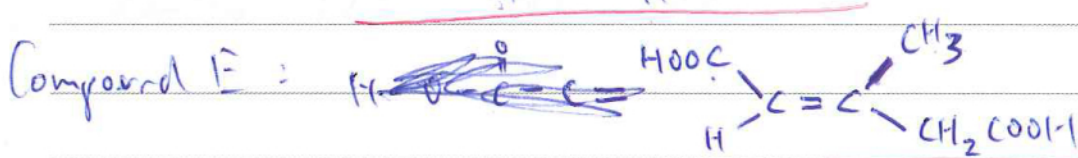
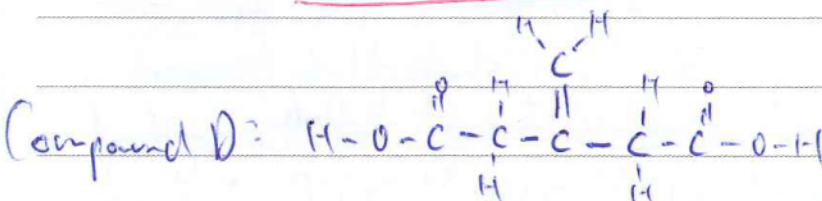
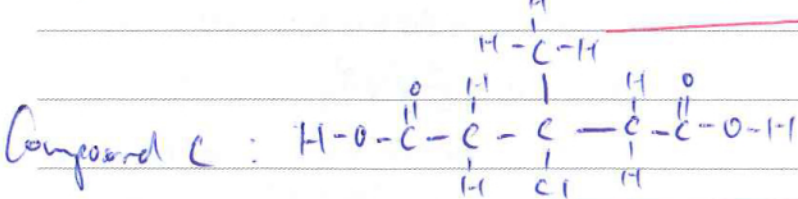
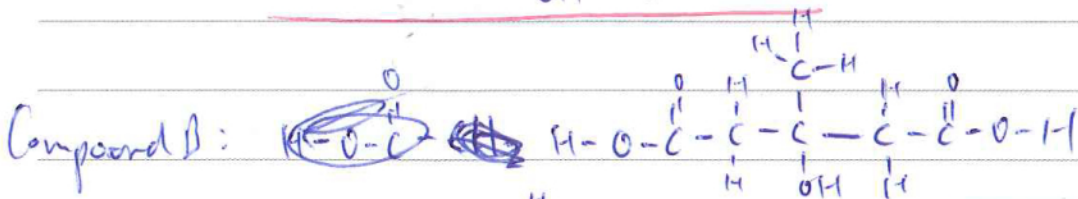
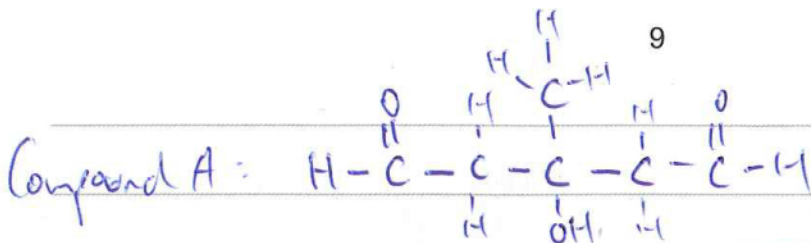


An acid anhydride where R_1 and R_2 can be the same or different alkyl groups.

Draw the structural formulae for the compounds **A** to **H** described below.

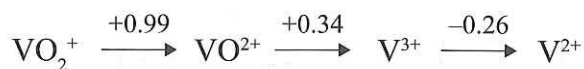
- Compound **A** has the molecular formula $\text{C}_6\text{H}_{10}\text{O}_3$. Compound **A** does not have enantiomers (optical isomers).
- Reaction of compound **A** with acidified potassium dichromate solution results in compound **B**, $\text{C}_6\text{H}_{10}\text{O}_5$.
- Reaction of compound **B** with anhydrous zinc chloride in concentrated hydrochloric acid produces compound **C**, $\text{C}_6\text{H}_9\text{O}_4\text{Cl}$.
- Compound **C**, reacts with alcoholic potassium hydroxide, followed by acidification, to produce compounds **D**, **E** and **F**, $\text{C}_6\text{H}_8\text{O}_4$. Compound **D** does not have stereoisomers, but compounds **E** and **F** are geometric isomers of each other.
- When compounds **D** and **F** are heated, two different compounds, **G** and **H**, with the molecular formula $\text{C}_6\text{H}_6\text{O}_3$, are produced. Compound **E** does not react on heating.





QUESTION THREE

- (a) Vanadium is a transition metal that exhibits a range of oxidation states. These are summarised in the Latimer diagram below, which includes the standard electrode potentials (in volts) for reduction of successive vanadium species. Values are given for pH = 0.



- (i) Compare the relative oxidising and reducing strengths of the four ions listed above.

The ~~red~~ reduction potentials of ($\text{VO}_2^+/\text{VO}^{2+}$) half cell is greater than ($\text{VO}^{2+}/\text{V}^{3+}$), which is greater than ($\text{V}^{3+}/\text{V}^{2+}$). This means that the ~~red~~ oxidation strength ~~of~~ from strongest to weakest is $\text{VO}_2^+ > \text{VO}^{2+} > \text{V}^{3+} > \text{V}^{2+}$ while the reduction strength is $\text{V}^{2+} > \text{V}^{3+} > \text{VO}^{2+} > \text{VO}_2^+$

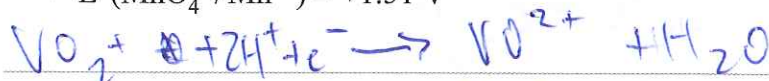
- (ii) Ammonium vanadate, NH_4VO_3 , in acidic solution contains the VO_2^+ ion. A 25.00 mL sample of acidified 0.09243 mol L⁻¹ ammonium vanadate solution was reacted with SO_2 . After boiling off any excess reductant, a blue solution remained. This blue solution required 21.38 mL of 0.0216 mol L⁻¹ acidified KMnO_4 to give a pink colour to the solution.

Another 25.00 mL portion of the ammonium vanadate solution was shaken with a zinc amalgam to give a violet coloured solution. This solution was titrated under an inert atmosphere with the KMnO_4 solution. 64.14 mL was required to reach the end point.

Account for these observations.

Include your titration calculations and a discussion on the relative reduction potentials of the reacting species.

$$E^\circ(\text{MnO}_4^-/\text{Mn}^{2+}) = +1.51 \text{ V}$$



$$n(\text{VO}_2^+) = 2.31 \times 10^{-3} \text{ mol} \quad n(\text{VO}^{2+}) = 2.31 \times 10^{-3} \text{ mol}$$

$$n(\text{KMnO}_4) = 4.62 \times 10^{-4} \text{ mol}$$

V has O.N of +4 in VO^{2+} and +5 in VO_2^+ .



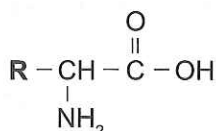
The number of moles of MnO_4^- is $\frac{1}{5}$ that of $n(\text{VO}_2^+)$, which suggests that ~~VO₂⁺~~ VO_2^+ was ~~reduced~~ ~~oxidised~~ only to VO^{2+} and not to V^{3+} because ~~only is the~~ ~~since the number~~ more MnO_4^- would have been used up to oxidise V^{3+} to VO_2^+ than the observed result. This means that the ~~SO₂/SO₄²⁻~~ $(\text{SO}_4^{2-}/\text{SO}_2)$ half cell has a reduction potential greater than +0.34 but lower than +0.99 as it can reduce VO_2^+ to VO^{2+} but not VO^{2+} to V^{3+} . The blue solution observed is the solution of VO^{2+} .

- (iii) An alternative to using an inert atmosphere for the second titration described in (ii) is to quickly decant the violet solution into an excess of the ammonium vanadate solution. The titration with KMnO_4 then proceeds as described, using the same volume of permanganate to reach the end point.

Explain why this alternative procedure is useful and why the same volume of KMnO_4 solution is needed.

This is done to make sure that any of the ~~ammonium~~ violet solution that reacts with air will immediately react with the excess ammonium vanadate solution to return to the violet solution. and will mean that the number of moles of the violet substance remains the same, so the same volume of KMnO_4 is needed.

- (b) Proteins are polymers of amino acids that contain different side chains, indicated as **R** in the diagram below. The properties of proteins are largely determined by the sequence of the amino acids from which they are made.



The table below shows some of the **R** groups of the amino acids that make up proteins.

Amino acid	Side chain (R)	pK_a of side chain (where appropriate)
alanine	$-\text{CH}_3$	
aspartic acid	$-\text{CH}_2\text{CO}_2\text{H}$	4
glutamic acid	$-\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$	4
leucine	$-\text{CH}_2\text{CH}(\text{CH}_3)_2$	
lysine	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+$	11
serine	$-\text{CH}_2\text{OH}$	

Classify, with reasons, whether the amino acid side chains in the table are charged, polar, or non-polar at physiological pH (7.4).

Discuss how the nature of each side chain could affect the observed tendency of proteins to fold up in aqueous solution.

Alanine side chain is non polar due to ~~the~~ little electronegativity difference between the ~~C~~ C and H in the C-H bond.

The pKa of aspartic acid is 4, so at pH = 7.4, the ratio of the conjugate ^{base} acid to aspartic acid is:

$7.4 - 4 = \log \left(\frac{[A^-]}{[HA]} \right) \frac{[A^-]}{[HA]} = 2512$. Most of the acid has converted to ~~base~~ base at this pH, which are ^{negatively} charged.

Glutamic acid has the same pKa of 4, so at pH = 7.4, most of the acid has converted to base so glutamic acid side chain is also ^{positively} negatively charged at pH = 7.4.

Leucine is non-polar as it only contains C-H and C-C bonds which are ~~are~~ not polar bonds.

Lysine has pKa of 11, so at pH = 7.4 the ratio of acid to base is: $7.4 - 11 = \log \frac{[A^-]}{[HA]}$

$\frac{[A^-]}{[HA]} = 2.52 \times 10^{-11}$. ~~HA is present~~ Acid is present in the vast majority at pH = 7.4. The acid is ^{positively} charged, so the lysine side chain is also ^{positively} charged.

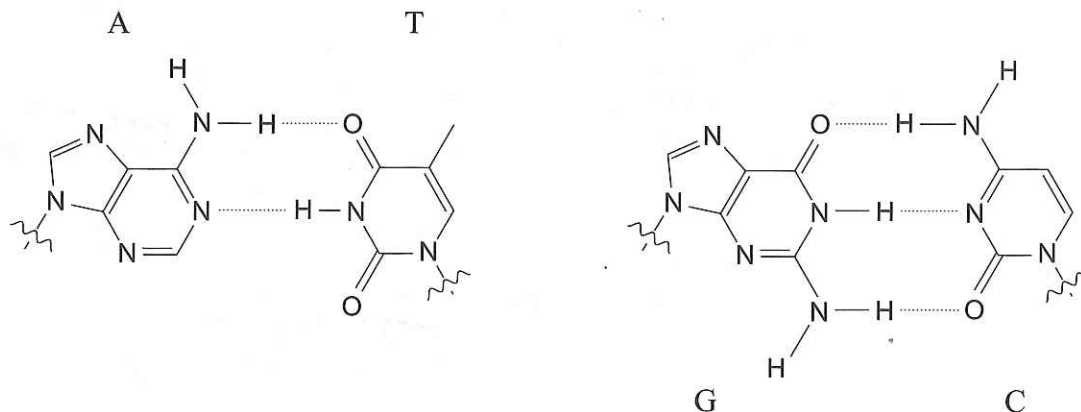
Serine is polar, as there is a large electronegativity between C ^{and}, O ^{and}, H ^{and} O so the C-O and ~~H~~ O-H bonds are polar covalent bonds. so dipoles are formed with slight positive charge on C and H in the O-H bond and slight negative charge on O.

Continued on extra paper.

QUESTION FOUR

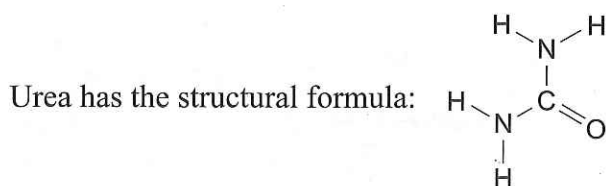
- (a) DNA is an alternating polymer of deoxyribose sugars and phosphate groups, with DNA bases (often labelled A, T, C, and G) attached to the sugar units.

DNA usually exists as two strands that are linked to each other by hydrogen bonds between the bases in the different strands: A with T, and G with C, as shown below.



Separation of the two strands can be achieved by heating aqueous solutions of the DNA.

If urea is present, DNA strands can be separated at lower temperatures.



The separation temperature for a range of DNA fragments in aqueous solutions is given in the table below (the first and last two base pairs are the same in all cases).

	DNA Fragment	Separation Temperature (°C)
1	$\begin{array}{cccccccc} \text{G} & - \text{G} & - \text{C} & - \text{C} & - \text{G} & - \text{G} & - \text{C} & - \text{C} \\ & & & & & & & \\ \text{C} & - \text{C} & - \text{G} & - \text{G} & - \text{C} & - \text{C} & - \text{G} & - \text{G} \end{array}$	32
2	$\begin{array}{cccccccc} \text{G} & - \text{G} & - \text{C} & - \text{C} & - \text{A} & - \text{T} & - \text{G} & - \text{G} & - \text{C} & - \text{C} \\ & & & & & & & & & \\ \text{C} & - \text{C} & - \text{G} & - \text{G} & - \text{T} & - \text{A} & - \text{C} & - \text{C} & - \text{G} & - \text{G} \end{array}$	36
3	$\begin{array}{cccccccc} \text{G} & - \text{G} & - \text{C} & - \text{C} & - \text{G} & - \text{C} & - \text{G} & - \text{G} & - \text{C} & - \text{C} \\ & & & & & & & & & \\ \text{C} & - \text{C} & - \text{G} & - \text{G} & - \text{C} & - \text{G} & - \text{C} & - \text{C} & - \text{G} & - \text{G} \end{array}$	40
4	$\begin{array}{cccccccc} \text{G} & - \text{G} & - \text{C} & - \text{C} & - \text{A} & - \text{A} & - \text{T} & - \text{T} & - \text{G} & - \text{G} & - \text{C} & - \text{C} \\ & & & & & & & & & & & \\ \text{C} & - \text{C} & - \text{G} & - \text{G} & - \text{T} & - \text{T} & - \text{A} & - \text{A} & - \text{C} & - \text{C} & - \text{G} & - \text{G} \end{array}$	40
5	$\begin{array}{cccccccc} \text{G} & - \text{G} & - \text{C} & - \text{C} & - \text{C} & - \text{A} & - \text{A} & - \text{G} & - \text{G} & - \text{G} & - \text{C} & - \text{C} \\ & & & & & & & & & & & \\ \text{C} & - \text{C} & - \text{G} & - \text{G} & - \text{G} & - \text{T} & - \text{T} & - \text{C} & - \text{C} & - \text{C} & - \text{G} & - \text{G} \end{array}$	44
6	$\begin{array}{cccccccc} \text{G} & - \text{G} & - \text{C} & - \text{C} & - \text{C} & - \text{A} & - \text{T} & - \text{G} & - \text{G} & - \text{G} & - \text{C} & - \text{C} \\ & & & & & & & & & & & \\ \text{C} & - \text{C} & - \text{G} & - \text{G} & - \text{G} & - \text{T} & - \text{A} & - \text{C} & - \text{C} & - \text{C} & - \text{G} & - \text{G} \end{array}$	44

Account for variations in the separation temperatures of the DNA fragments, AND discuss the reasons for the decrease in the separation temperature when urea is present.

Fragment 1 has the lowest separation temperature as it is the shortest chain so less bonds has to be broken thus lower temperature needed.

Fragment 2 has 2 A-T ~~fragments~~ links ^{and the rest C-G} while Fragment 3 has only C-G links. ~~the C-G links~~ C forms 3 hydrogen bonds with G, while A only forms 2 hydrogen bonds with T. This means the C-G bond takes more energy to break than the A-T bond, so fragment 3 has a higher separation temperature despite being of the same length as fragment 2.

Similarly, fragment 4 has lower separation temperature than 5 and 6 as fragment 4 has more A-T bonds while ^{having} ~~being~~ the same length. The difference between 5 and 6 is that one has ~~A~~ one A and one T on each antiparallel strand while the other has 2 As ~~and 2 Ts~~ on one strand next to each other and the other has 2 Ts. This makes no difference to the strength of the bonding of the A-T bond. Since 5 and 6 has the same number of C-G bonds and A-T bonds, their separation temperature is the same at 44°C .

Urea is a molecule that can form many hydrogen bonds due to the N-H bond and the highly electronegative ~~O~~ C=O bond. This means that urea will form hydrogen bonding with the DNA bases instead of the bases forming bonds with each other. This will weaken the overall strength of the molecule of DNA due to less hydrogen bonding so the separation temperature is lower.

- (b) The amount of carbon dioxide in the atmosphere is increasing due to the combustion of fossil fuels. The concentration of a dissolved gas in a solution is directly proportional to the partial pressure of that gas above the solution. This means that increasing the carbon dioxide in the Earth's atmosphere will increase the amount of dissolved carbon dioxide in the oceans. The concentration of carbonate ions, utilised by shell-forming organisms to form CaCO_3 , varies with the amount of dissolved CO_2 . This, in turn, affects the availability of dissolved calcium ions.

Information

- $\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{aq})$
- Solubility of CO_2 in water obeys Henry's Law: $\frac{[\text{CO}_2(\text{aq})]}{P_{\text{CO}_2}} = K_h$,
where P_{CO_2} is the partial pressure of CO_2 in the atmosphere.
- Henry's Law constant for CO_2 at 25°C , is $3.317 \times 10^{-4} \text{ mol L}^{-1} \text{ kPa}^{-1}$.
- The current partial pressure of CO_2 in the atmosphere is 0.0397 kPa .
- Dissolved carbon dioxide reacts with the water to form carbonic acid:
 $\text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}) \quad K_1 = 1.70 \times 10^{-3}$
- H_2CO_3 is a weak acid: $\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}_3\text{O}^+ \quad K_2 = 2.51 \times 10^{-4}$
- HCO_3^- also reacts with water: $\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{CO}_3^{2-} + \text{H}_3\text{O}^+ \quad K_3 = 5.62 \times 10^{-11}$
- CaCO_3 is a sparingly soluble salt $K_s = 4.8 \times 10^{-9}$
- The pH of the oceans is currently about 8.10.

Calculate the concentration of Ca^{2+} ions at the current pH of the ocean, using the data given above.

$$[\text{CO}_2] = k_h \times P_{\text{CO}_2} = 1.316849 \times 10^{-5} \text{ mol L}^{-1}$$

$$\frac{[\text{H}_2\text{CO}_3]}{[\text{CO}_2]} = 1.70 \times 10^{-3} \quad [\text{H}_2\text{CO}_3] = 2.2386 \times 10^{-8} \text{ mol L}^{-1}$$

$$2.51 \times 10^{-4} = \frac{[\text{HCO}_3^-] \times [\text{H}_3\text{O}^+]}{[\text{H}_2\text{CO}_3]}$$

$$\text{pH} = 8.10$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 7.94 \times 10^{-9} \text{ mol L}^{-1}$$

$$[\text{HCO}_3^-] = 7.07668 \times 10^{-4} \text{ mol L}^{-1}$$

$$5.62 \times 10^{-11} = \frac{[\text{CO}_3^{2-}] \times [\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]}$$

$$[\text{CO}_3^{2-}] = \frac{5.62 \times 10^{-11} \times 7.07668 \times 10^{-4}}{7.94 \times 10^{-9}}$$

$$= 5.00686 \times 10^{-6} \text{ mol L}^{-1}$$

$$4.8 \times 10^{-9} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}]$$

$$[\text{Ca}^{2+}] = \frac{4.8 \times 10^{-9}}{5.00686 \times 10^{-6}}$$

$$= 9.59 \times 10^{-4} \text{ mol L}^{-1}$$

QUESTION FIVE

All
On ~~steps~~
extra paper

- (a) Discuss briefly why adding 70.0 mL of 0.400 mol L⁻¹ ethanoic acid (pK_a = 4.76) to 100.0 mL of 0.0200 mol L⁻¹ hydrochloric acid would not greatly change the pH of the original solution.

Justify your answer by including a calculation of the concentration, in mol L⁻¹, of ethanoate ions.

$$K_a = 10^{-4.76} = 1.7378 \times 10^{-5} \quad [\text{ethanoic acid}] = \frac{0.07 \times 0.4}{0.07 + 0.1} =$$

$$1.7378 \times 10^{-5} = \frac{[\text{ethanoate}]^2}{[\text{ethanoic acid}]}$$

$$[\text{ethanoate}] = 2.64 \times 10^{-3} \text{ mol L}^{-1}$$

~~pH~~ Original pH of HCl = $-\log(0.0200) = 1.70$

$$\text{New pH} = -\log\left(\frac{0.02 \times 0.1 + 2.64 \times 10^{-3} \times 0.07}{0.17}\right) = 1.89$$

The ~~concentration~~^{number} of H₃O⁺ added by the addition is ~~negligible~~^{about} less than a tenth of the ~~original~~^{number} of H₃O⁺ in the HCl solution. Only the addition of extra volume of water ~~changes~~^{changes} the pH by a ~~very~~^{small} amount.

- (b) (i) Carry out the appropriate calculations to enable you to sketch the titration curves for the following titrations on the grid provided.

Show your working for your calculations.

Titration 1: 40.00 mL of 0.0500 mol L⁻¹ NH₄Cl with 0.200 mol L⁻¹ NaOH (up to 20 mL)

Titration 2: 40.00 mL of 0.0500 mol L⁻¹ NH₃(aq) with 0.200 mol L⁻¹ HCl (up to 20 mL)

$$pK_a(\text{NH}_4^+) = 9.24$$

Calculation space:

$$\text{Titration 1: original pH} = \sqrt{\frac{10^{-9.24} \times 0.0500}{0.0500}} = 5.27$$

$$\text{half equivalence: } \text{pH} = \text{p}K_a = 9.24$$

$$\text{equivalence: } c(\text{NH}_3) = \frac{0.05 \times 4}{5} = 0.0400$$

$$\text{pH} = 10.92$$

$$20 \text{ mL excess: } [\text{OH}^-] = \frac{0.01 \times 0.200}{0.06}$$

$$\text{pH} = 12.52$$

$$\text{Titration 2: original pH} = \sqrt{\frac{K_w \times K_a}{0.0500}} = 10.97$$

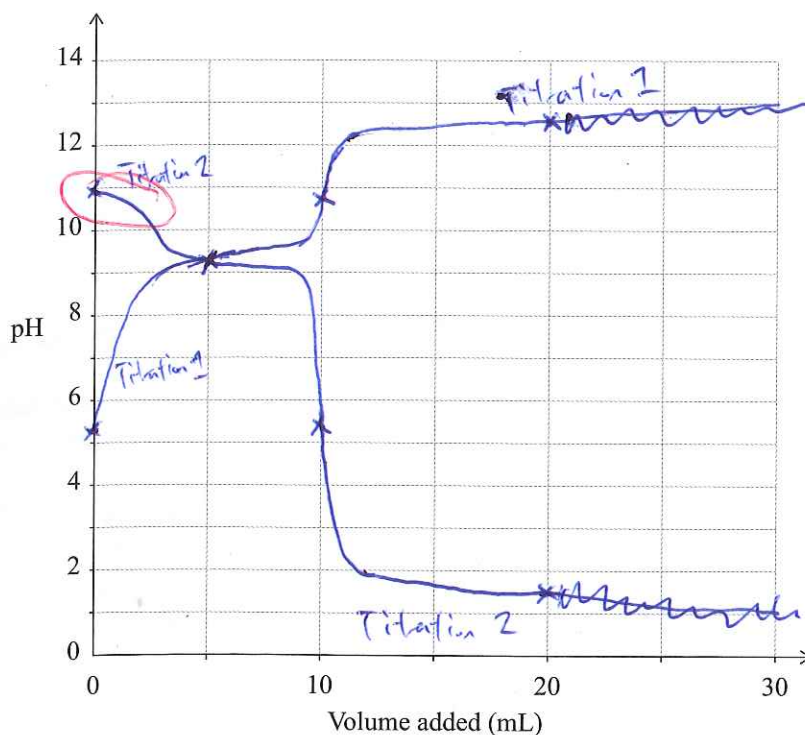
$$\text{half equivalence } \text{pH} = \text{p}K_a$$

$$\text{equivalence } \text{pH} = -\log \left(\frac{10^{-9.24}}{0.04} \right)$$

$$= -\log(10^{-9.24} \times 0.04) = 5.32$$

$$10 \text{ mL excess } [\text{H}_3\text{O}^+] = \frac{0.01 \times 0.200}{0.06}$$

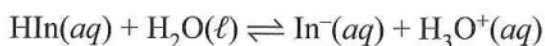
$$\text{pH} = 1.48$$



- (ii) Discuss the similarities and differences between the two curves in terms of the species present in the titration solutions.

The difference between the original pH of the solution and ^{half} equivalence pH is based on the strength of the NH_4^+ and NH_3 . NH_4^+ is a weaker acid than NH_3 ^{strength as a base} ~~is a base~~ so the NH_4^+ is further from the ~~equilibrium~~ half equilibrium pH. NH_4^+ starts off pH ~~above~~ below 7 as it is an acid while NH_3 starts off ~~at~~ above 7 as it is a base. At half equivalence, the pH of both solutions are the same since both contain equal concentrations of NH_3 and NH_4^+ . In titration 1, the equivalence point ~~at~~ pH is above 7 as ~~now~~ ~~the solution contains~~ all of the NH_4^+ has converted to NH_3 , a base while ~~the opposite~~ in titration 2, all of the NH_3 has converted to NH_4^+ , an acid. In titration 1, the pH continues to grow ~~due to~~ slowly after ~~the~~ excess NaOH due to addition of strong base while in titration 2, addition of excess HCl causes the pH to drop slowly.

- (c) An indicator is usually a weak acid or base that has different colours in its neutral or ionic forms. The pK_a of an indicator can be used to determine its usefulness in a titration. For the indicator HIn:



When methyl red is used as an indicator for the titration of NH_3 with HCl (as described in (b)(i)), the initial colour of the indicator is yellow, and after 15.00 mL of HCl has been added, it is red. The end point of the titration is indicated by an orange colour. It is easier to observe this colour change when the colour is intensified by using more than a few drops of indicator.

$$pK_a(\text{methyl red}) = 5.1$$

Discuss the colour changes that are observed during this titration, relating these to the different forms of the indicator that are present AND explain any consequences for the accuracy of a titration of using more than a few drops of indicator.

The solution is initially 10.97 pH which is basic so almost all of the ~~base~~ methyl red is present as In^- which is yellow. As HCl is added, the pH of the solution decreases and the concentration of HIn also increases while In^- decreases, but this is not a noticeable colour change due to a ~~overwhelming~~ majority of In^- before equivalence point. At the equivalence point of the titration, which is close to the pK_a (methyl red), there is an equal ^{concentration} ~~number~~ of In^- (which are yellow) and HIn (which are red) so a ~~change~~ change to orange in the solution colour is seen. At excess of HCl , the solution is highly acidic, so there is mostly HIn in solution, which makes the solution red.

If ~~too much~~ indicator is added ^{OH^-} the indicator is a weak acid ~~base~~ which contributes some ~~H_3O^+~~ to solution as it changes to In^- . If too much indicator is added, the ~~H_3O^+~~ ^{HIn} contribution

OH^- contribution will be great enough that it will change the pH of the solution significantly enough that the equivalence point is changed as ~~if~~ more HCl is added to ~~deprotonate~~ protonate In^- instead of just

Extra paper if required.

Write the question number(s) if applicable.

ASSESSOR'S
USE ONLYQUESTION
NUMBER

$$\text{Qa } [\text{ethanoic acid}] = \frac{0.4 \times 0.07}{0.17} = 0.1647 \text{ mol L}^{-1}$$

$$K_a = 10^{-4.76} = 1.7378 \times 10^{-5}$$

$$1.7378 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+] \times [\text{ethanoate}]}{[\text{ethanoic acid}]}$$

$$[\text{H}_3\text{O}^+] = \frac{0.0200 \times 0.1}{0.17} = 0.0117647 \text{ mol L}^{-1}$$

$$[\text{ethanoate}] = \frac{1.7378 \times 10^{-5} \times 0.1647}{0.0117647}$$

$$= 2.43 \times 10^{-4} \text{ mol L}^{-1}$$

The ethanoic acid is in equilibrium with ethanoate and H^+ . The ethanoic acid is added to HCl solution, which contains a ~~large~~ large concentration of ~~H~~ H^+ from HCl. This large concentration of a product means that ~~the~~ equilibrium shifts to favour the reverse reaction of



which means the contribution of H^+ by CH_3COOH is very insignificant. The pH change seen is mostly due to the added water volume, which decreases concentration of H_3O^+ .

Extra paper if required.

Write the question number(s) if applicable.

ASSESSOR'S
USE ONLYQUESTION
NUMBER

3b ~~The charged ends of the side chains are attracted to~~
In aqueous solution, if the pH is not 7.4 but much
higher or lower, the ~~the~~ normally charged ends
of ~~the side~~ some of the side chains could ~~become~~
turn into its uncharged form. This will mean that
the water molecules around the protein are not attracted
to the ends of the side chains and so the proteins fold
up as a result. ✓

seen.